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Synthesis and crystal structure of 5-carbaphosphatranes containing a four-membered cycle

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Solvents and commercially available reagents were purified by conventional methods before use. All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. Measurements involved "Boetius" melting point apparatus (manufacturing of DDR). NMR experiments were performed in $CDCl_3$ at 20°C with Varian Unity-300 spectrometer (^{31}P, ^{31}P-{^1H} 121.42 MHz, ^{19}F, 282.4 MHz) and with a Bruker AVANCE-600 spectrometer with a 5 mm diameter inverse probe head with Z-active shielded gradients working at 600.000 MHz in ^1H, 150.864 MHz in ^{13}C. The δ_H and δ_P values were determined relative to internal (HMDS) or external (H_3PO_4) standard. The δ_F values were determined relative to internal standard (C_6F_6) and then recalculated relative to $CFCl_3$. The δ_C values were determined relative to the deuterated solvent signal. Complete assignment of the ^1H and ^{13}C NMR spectra of the title compounds were accomplished by DEPT, 2D COSY, HSQC, HMBC experiments. IR spectra were registered on Specord M-80 Instrument in Nujol. EI mass spectra were obtained with a TRACE MS Finnigan MAT instrument; the ionization energy was 70 eV and the ion source temperature was 200°C. The samples were introduced into the ion source *via* a direct inlet system. The evaporating ampoule was heated from 35 to 150°C at a rate of 35°C min^{-1}. The mass spectrometric data were processed using the Xcalibur system program.

4,4-Bis(trifluoromethyl)-4,5-dihydro-2-phenylbenzo[e]-1,3,2-dioxaphosphepin-5-one **3**. A solution of dichlorophenylphosphine (5.48 g, 0.031 mol) in ether (30 ml) was added dropwise to the mixture of 2'-hydroxyphenyl-(1-hydroxy-2,2,2-trifluoro-1-trifluoromethyl)ethyl ketone **1** (8.82 g, 0.031 mol), triethylamine (6.2 g, 0.061 mol) and ether (150 ml) at –30 °C in argon atmosphere. Obtained mixture was stirred 1.5 h (the temperature was allowed to reach 20 °C) and was left overnight. The forming precipitate of triethylammonium chloride was filtered and the residue was dried in vacuum (20°C, 0.1 mmHg). Yield of compound **3** is 91 %, m.p. 105-107 °C (decom.). ^{19}F NMR ($CDCl_3$): δ_F –73.57 dq (CF^A_3, $^4J_{POCCF}{}^A$ 20.5 Hz, $^4J_F{}^B{}_{CCCF}{}^A$ 9.2 Hz), δ_F –74.13

qd (CF^{B}_{3}, $^{4}J_{F}{}^{A}{}_{CCCF}{}^{B}$ 9.2 Hz, $^{4}J_{POCCF}{}^{B}$ 2.3 Hz). ^{31}P NMR (121.42 MHz, $CDCl_3$): δ_P 173.1 qq ($^{4}J_{POCCF}{}^{A}$ 20.7 Hz, $^{4}J_{POCCF}{}^{B}$ 2.5 Hz). IR (cm^{-1}): 1684, 1600, 1444, 1288, 1164, 1128, 1064, 976, 896, 872, 776, 744, 712, 689.

4,4-Bis(trifluoromethyl)-4,5-dihydro-2-phenyl-(4'-chlorobenzo)[e]-1,3,2-dioxaphosphepin-5-one **4** was obtained similar to compound **3** from ketone **2** and dichlorophenylphosphine. Yield 86 %, m.p. 151 °C (decom.). ^{19}F NMR ($CDCl_3$): δ_F –69.8 (CF_3, m), δ_F –70.0 (CF_3, m). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P 174.8 br. q ($^{4}J_{POCCF}$ 18.3 Hz). IR (cm^{-1}): 1696, 1596,1576 1468, 1420, 1392, 1312, 1128, 1060, 980,932, 860, 840, 816, 800, 776, 752, 736, 716, 696, 652, 536.

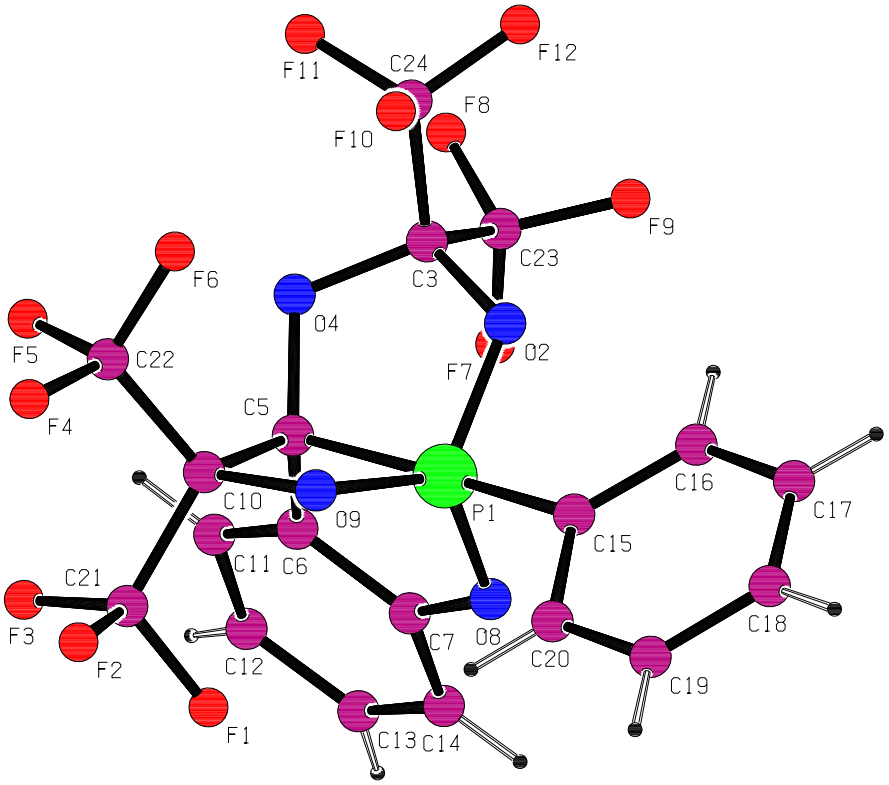

Figure 1. Molecular geometry of compound **5** in a crystal.

Bond length	***d*, Å**	**Bond length**	***d*, Å**	**Bond length**	***d*, Å**
P^1–O^8	1.623(2)	F^9–C^{23}	1.317(4)	C^6–C^5	1.487(4)
P^1–O^2	1.649(3)	F^{10}–C^{24}	1.303(4)	C^{20}–C^{19}	1.378(5)
P^1–O^9	1.670(2)	F^6–C^{22}	1.314(5)	C^{20}–C^{15}	1.383(5)
P^1–C^{15}	1.804(3)	O^4–C^3	1.416(4)	C^{12}–C^{13}	1.372(6)
P^1–C^5	1.879(3)	O^4–C^5	1.418(4)	C^{12}–C^{11}	1.395(5)
F^2–C^{21}	1.330(4)	O^2–C^3	1.388(3)	C^{24}–C^3	1.545(5)
F^1–C^{21}	1.332(4)	O^9–C^{10}	1.435(4)	C^{15}–C^{16}	1.385(5)
F^3–C^{21}	1.320(4)	O^8–C^7	1.410(4)	C^{16}–C^{17}	1.383(5)
F^{12}–C^{24}	1.317(5)	C^{10}–C^{21}	1.519(5)	C^3–C^{23}	1.551(5)
F^7–C^{23}	1.307(5)	C^{10}–C^{22}	1.539(4)	C^{13}–C^{14}	1.382(5)
F^4–C^{22}	1.315(4)	C^{10}–C^5	1.561(4)	C^7–C^{14}	1.380(4)
F^{11}–C^{24}	1.322(4)	C^6–C^{11}	1.377(4)	C^{19}–C^{18}	1.362(6)
F^5–C^{22}	1.324(4)	C^6–C^7	1.385(4)	C^{18}–C^{17}	1.366(6)

Bond angle	**φ, grad.**	**Bond angle**	**φ, grad.**	**Bond angle**	**φ, grad.**
O^8–P^1–O^2	116.9(1)	F^{10}–C^{24}–F^{12}	106.9(3)	O^2–C^3–C^{23}	108.5(3)
O^8–P^1–O^9	122.6(1)	F^{10}–C^{24}–F^{11}	107.7(3)	O^4–C^3–C^{23}	109.4(3)
O^2–P^1–O^9	119.0(1)	F^{12}–C^{24}–F^{11}	107.6(3)	C^{24}–C^3–C^{23}	111.1(3)
O^8–P^1–C^{15}	93.7(1)	F^{10}–C^{24}–C^3	111.7(3)	C^{12}–C^{13}–C^{14}	122.3(3)
O^2–P^1–C^{15}	94.8(1)	F^{11}–C^{24}–C^3	111.4(3)	C^{14}–C^7–C^6	122.7(3)
O^9–P^1–C^{15}	94.2(1)	C^{20}–C^{15}–C^{16}	118.1(3)	C^{14}–C^7–O^8	120.9(3)
O^8–P^1–C^5	91.7(1)	C^{20}–C^{15}–P^1	118.8(3)	C^6–C^7–O^8	116.4(3)
O^2–P^1–C^5	88.3(1)	C^{16}–C^{15}–P^1	123.0(3)	C^7–C^{14}–C^{13}	116.3(3)
O^9–P^1–C^5	77.6(1)	O^4–C^5–C^6	115.6(2)	C^6–C^{11}–C^{12}	118.0(3)
C^{15}–P^1–C^5	171.7(1)	O^4–C^5–C^{10}	113.9(2)	C^{18}–C^{19}–C^{20}	120.6(4)
C^3–O^4–C^5	110.1(2)	C^6–C^5–C^{10}	120.0(3)	C^{19}–C^{18}–C^{17}	119.8(4)
C^3–O^2–P^1	117.3(2)	O^4–C^5–P^1	108.7(2)	C^{18}–C^{17}–C^{16}	120.1(4)
C^{10}–O^9–P^1	99.2(2)	C^6–C^5–P^1	107.1(2)	F^7–C^{23}–F^9	106.8(3)
C^7–O^8–P^1	114.8(2)	C^{10}–C^5–P^1	86.6(2)	F^7–C^{23}–F^8	109.2(3)
O^9–C^{10}–C^{21}	107.6(3)	C^{17}–C^{16}–C^{15}	120.7(4)	F^9–C^{23}–F^8	106.8(3)
O^9–C^{10}–C^{22}	110.9(3)	F^3–C^{21}–F^2	108.0(3)	F^7–C^{23}–C^3	110.6(3)
C^{21}–C^{10}–C^{22}	109.6(3)	F^3–C^{21}–F^1	108.1(3)	F^9–C^{23}–C^3	111.9(3)
O^9–C^{10}–C^5	96.1(2)	F^2–C^{21}–F^1	105.8(3)	F^8–C^{23}–C^3	111.4(3)
C^{21}–C^{10}–C^5	116.0(3)	F^3–C^{21}–C^{10}	111.8(3)	F^6–C^{22}–F^4	107.1(3)
C^{22}–C^{10}–C^5	115.6(3)	F^2–C^{21}–C^{10}	111.4(3)	F^6–C^{22}–F^5	106.9(3)
C^{11}–C^6–C^7	120.0(3)	F^1–C^{21}–C^{10}	111.4(3)	F^4–C^{22}–F^5	107.8(3)
C^7–C^6–C^5	109.8(3)	O^2–C^3–O^4	112.0(2)	F^6–C^{22}–C^{10}	112.1(3)
C^{19}–C^{20}–C^{15}	120.7(4)	O^2–C^3–C^{24}	108.4(3)	F^4–C^{22}–C^{10}	112.7(3)
C^{13}–C^{12}–C^{11}	120.6(3)	O^4–C^3–C^{24}	107.5(3)	F^5–C^{22}–C^{10}	110.0(3)

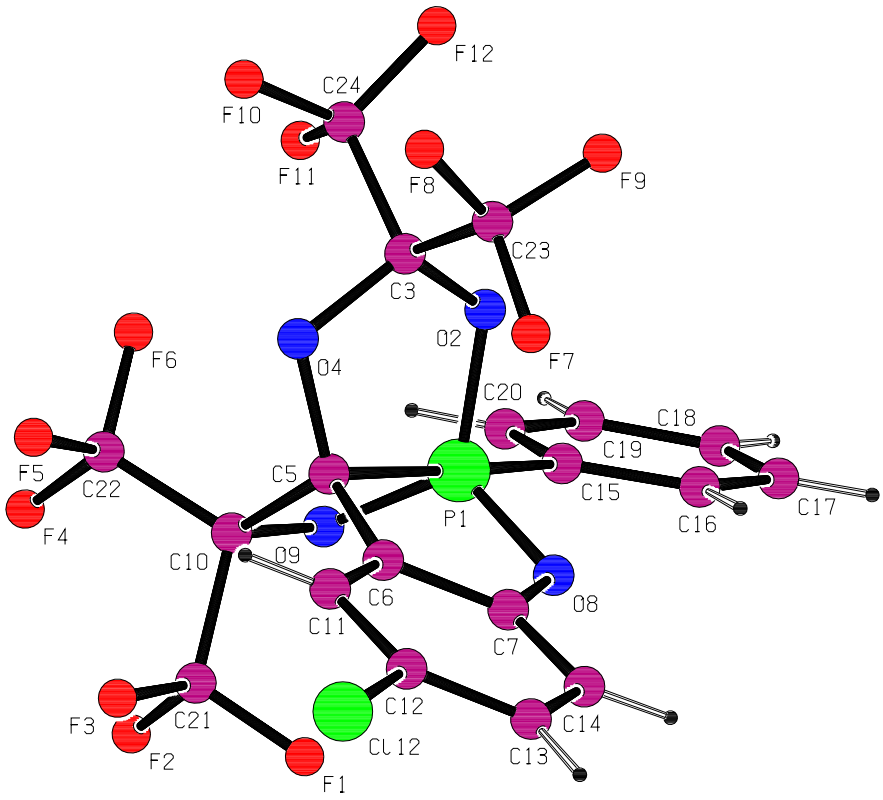

Figure 2. Molecular geometry of compound **6** in a crystal.

Bond length	***d*, Å**	**Bond length**	***d*, Å**	**Bond length**	***d*, Å**
$C^3–O^2$	1.398(4)	$C^{10}–C^{21}$	1.556(5)	$C^{21}–F^3$	1.323(5)
$C^3–O^4$	1.415(4)	$C^{10}–P^1$	2.370(4)	$C^{21}–F^2$	1.331(5)
$C^3–C^{23}$	1.543(5)	$C^{11}–C^{12}$	1.381(6)	$C^{22}–F^6$	1.317(5)
$C^3–C^{24}$	1.562(6)	$C^{12}–C^{13}$	1.384(6)	$C^{22}–F^4$	1.322(5)
$C^5–O^4$	1.436(4)	$C^{12}–Cl^{12}$	1.751(3)	$C^{22}–F^5$	1.329(5)
$C^5–C^6$	1.489(5)	$C^{13}–C^{14}$	1.407(5)	$C^{23}–F^7$	1.320(5)
$C^5–C^{10}$	1.546(5)	$C^{15}–C^{20}$	1.392(6)	$C^{23}–F^8$	1.323(5)
$C^5–P^1$	1.881(4)	$C^{15}–C^{16}$	1.392(6)	$C^{23}–F^9$	1.332(4)
$C^6–C^{11}$	1.388(5)	$C^{15}–P^1$	1.808(3)	$C^{24}–F^{11}$	1.314(5)
$C^6–C^7$	1.390(5)	$C^{16}–C^{17}$	1.403(5)	$C^{24}–F^{10}$	1.324(5)
$C^7–C^{14}$	1.359(6)	$C^{17}–C^{18}$	1.381(7)	$C^{24}–F^{12}$	1.336(4)
$C^7–O^8$	1.404(4)	$C^{18}–C^{19}$	1.376(7)	$O^2–P^1$	1.669(3)
$C^{10}–O^9$	1.440(4)	$C^{19}–C^{20}$	1.396(6)	$O^8–P^1$	1.623(3)
$C^{10}–C^{22}$	1.541(6)	$C^{21}–F^1$	1.319(5)	$O^9–P^1$	1.663(3)

Bond angle	φ, grad.	Bond angle	φ, grad.	Bond angle	φ, grad.
O^2–C^3–O^4	112.6(3)	C^{11}–C^{12}–C^{13}	122.9(3)	F^7–C^{23}–F^8	108.3(3)
O^2–C^3–C^{23}	109.5(3)	C^{11}–C^{12}–Cl^{12}	118.8(3)	F^7–C^{23}–F^9	107.9(3)
O^4–C^3–C^{23}	109.6(3)	C^{13}–C^{12}–Cl^{12}	118.3(3)	F^8–C^{23}–F^9	107.7(3)
O^2–C^3–C^{24}	106.9(3)	C^{12}–C^{13}–C^{14}	119.5(4)	F^7–C^{23}–C^3	110.2(3)
O^4–C^3–C^{24}	108.2(3)	C^7–C^{14}–C^{13}	117.5(4)	F^8–C^{23}–C^3	110.8(3)
C^{23}–C^3–C^{24}	110.0(3)	C^{20}–C^{15}–C^{16}	119.2(3)	F^9–C^{23}–C^3	111.8(3)
O^4–C^5–C^6	115.4(3)	C^{20}–C^{15}–P^1	119.8(3)	F^{11}–C^{24}–F^{10}	109.2(4)
O^4–C^5–C^{10}	113.8(3)	C^{16}–C^{15}–P^1	121.0(3)	F^{10}–C^{24}–F^{12}	108.1(3)
C^6–C^5–C^{10}	120.1(3)	C^{15}–C^{16}–C^{17}	120.1(4)	F^{11}–C^{24}–C^3	111.1(3)
O^4–C^5–P^1	108.8(2)	C^{18}–C^{17}–C^{16}	119.8(4)	F^{10}–C^{24}–C^3	110.6(3)
C^6–C^5–P^1	107.1(3)	C^{19}–C^{18}–C^{17}	120.5(4)	F^{12}–C^{24}–C^3	110.6(3)
C^{10}–C^5–P^1	86.9(2)	C^{18}–C^{19}–C^{20}	120.0(4)	C^3–O^2–P^1	116.7(2)
C^{11}–C^6–C^7	120.4(3)	C^{15}–C^{20}–C^{19}	120.4(4)	C^3–O^4–C^5	109.3(3)
C^{11}–C^6–C^5	129.9(3)	F^1–C^{21}–F^3	109.3(4)	C^7–O^8–P^1	115.0(2)
C^7–C^6–C^5	109.6(3)	F^1–C^{21}–F^2	105.7(3)	C^{10}–O^9–P^1	99.3(2)
C^{14}–C^7–C^6	122.8(3)	F^3–C^{21}–F^2	107.6(4)	O^8–P^1–O^9	119.4(2)
C^{14}–C^7–O^8	120.8(3)	F^1–C^{21}–C^{10}	111.3(3)	O^8–P^1–O^2	115.0(2)
C^6–C^7–O^8	116.4(3)	F^3–C^{21}–C^{10}	111.2(3)	O^9–P^1–O^2	123.8(2)
O^9–C^{10}–C^{22}	110.8(3)	F^2–C^{21}–C^{10}	111.5(3)	O^8–P^1–C^{15}	95.7(2)
O^9–C^{10}–C^5	96.1(3)	F^6–C^{22}–F^4	106.7(4)	O^9–P^1–C^{15}	94.8(2)
C^{22}–C^{10}–C^5	116.5(3)	F^6–C^{22}–F^5	108.5(3)	O^2–P^1–C^{15}	93.0(1)
O^9–C^{10}–C^{21}	107.5(3)	F^4–C^{22}–F^5	107.9(3)	O^8–P^1–C^5	91.6(2)
C^{22}–C^{10}–C^{21}	110.1(3)	F^6–C^{22}–C^{10}	111.1(3)	O^9–P^1–C^5	77.4(2)
C^5–C^{10}–C^{21}	114.6(3)	F^4–C^{22}–C^{10}	113.1(3)	O^2–P^1–C^5	88.2(1)
C^{12}–C^{11}–C^6	116.9(3)	F^5–C^{22}–C^{10}	109.5(3)	C^{15}–P^1–C^5	171.3(2)

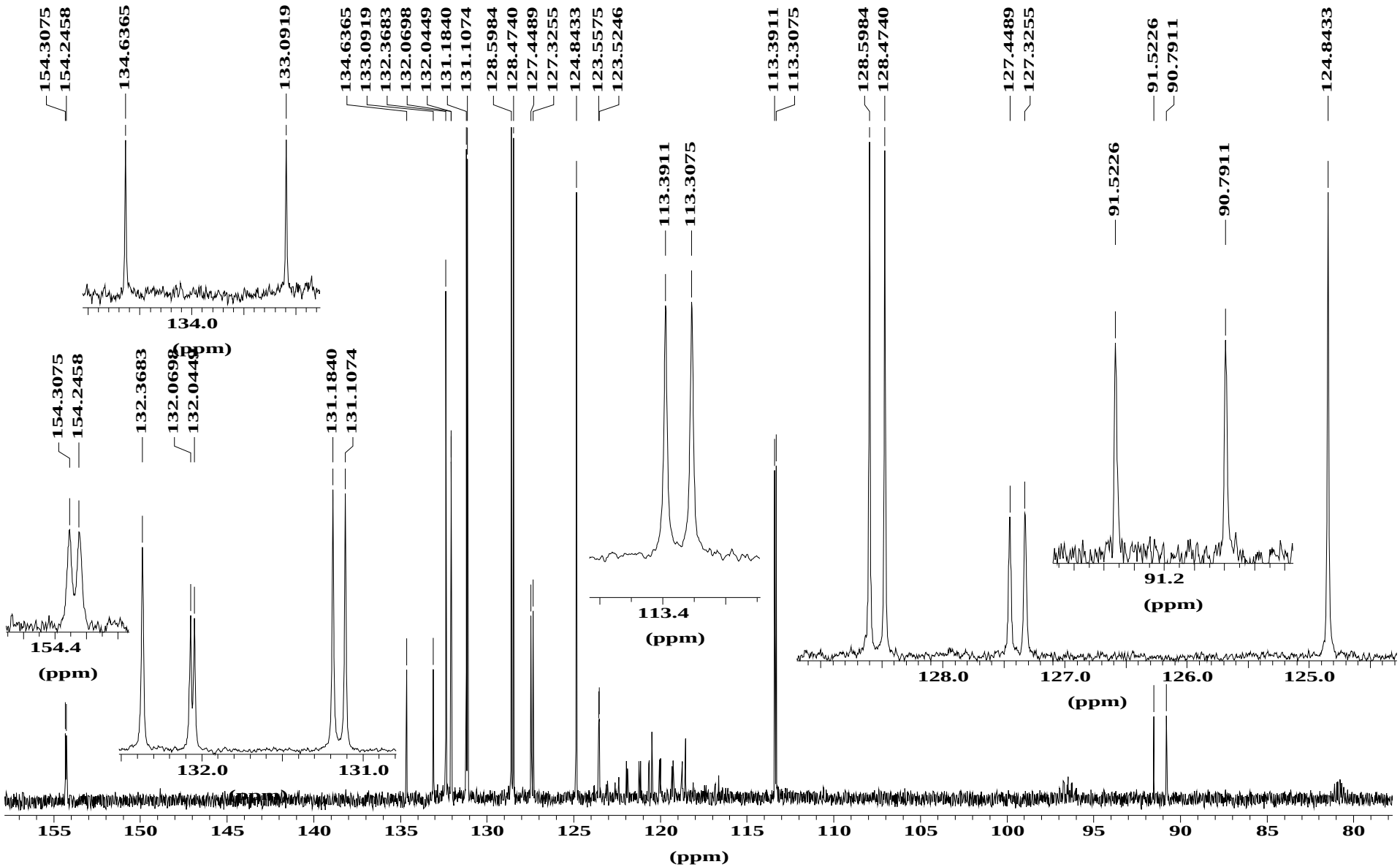

Fig. 1. ^{13}C-{^{1}H} NMR spectrum of compound **5** (150.9 MHz, $CDCl_3$).

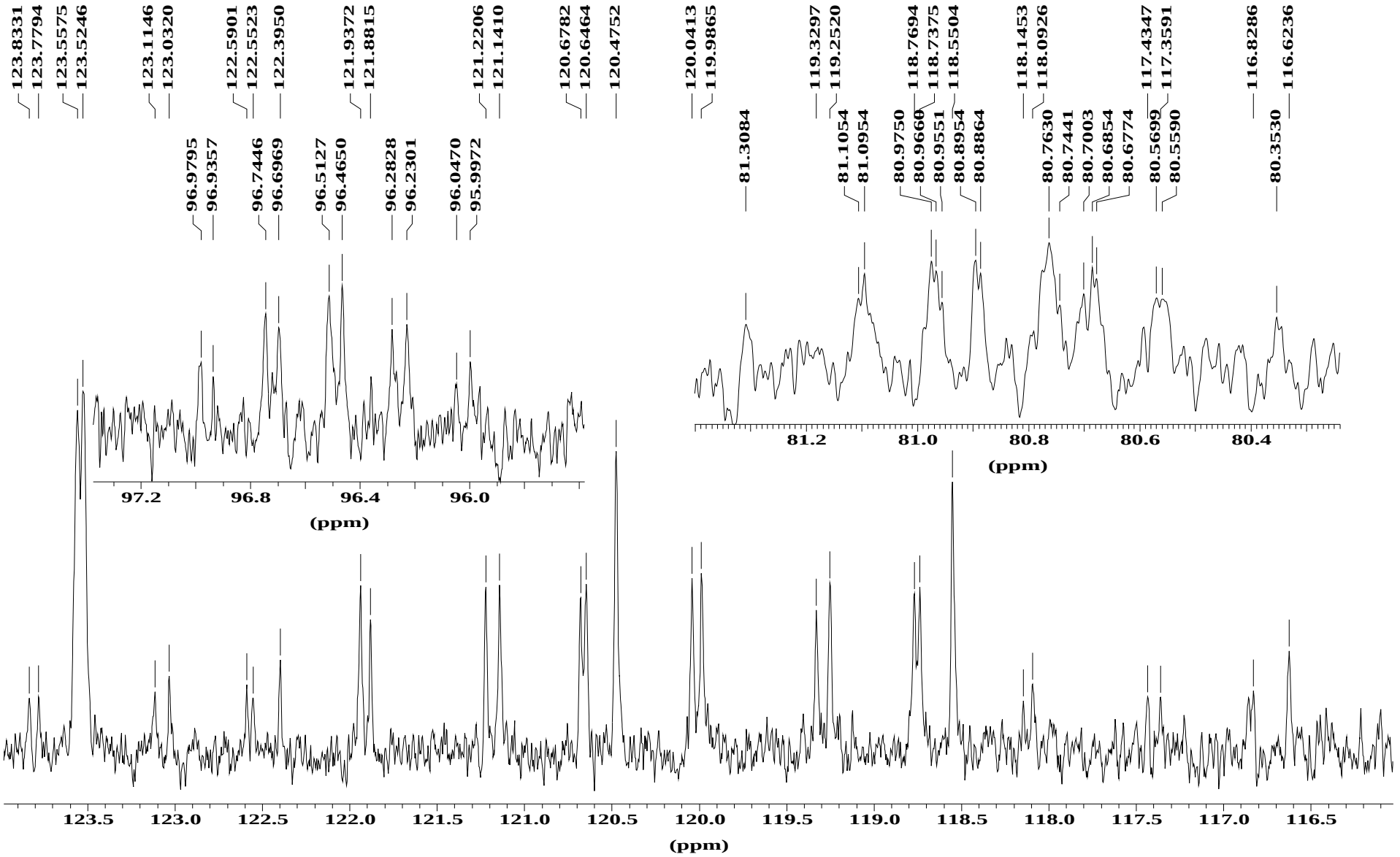

Fig. 2. Fragments of ^{13}C-{^{1}H} NMR spectrum of compound **5** (150.9 MHz, $CDCl_3$).

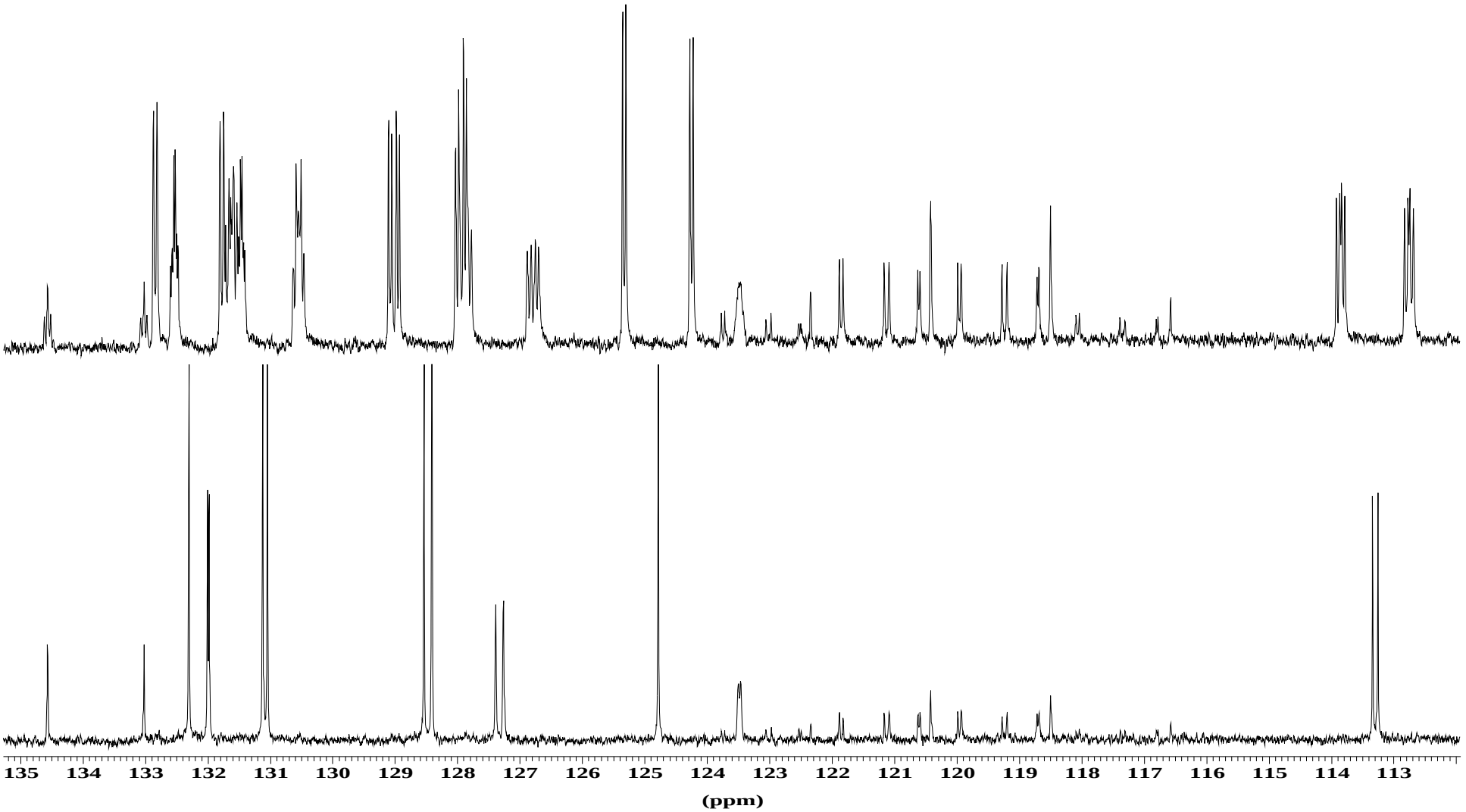

Fig. 3. Fragments of ^{13}C-{^{1}H} and ^{13}C NMR spectra of compound **5** (150.9 MHz, $CDCl_3$).

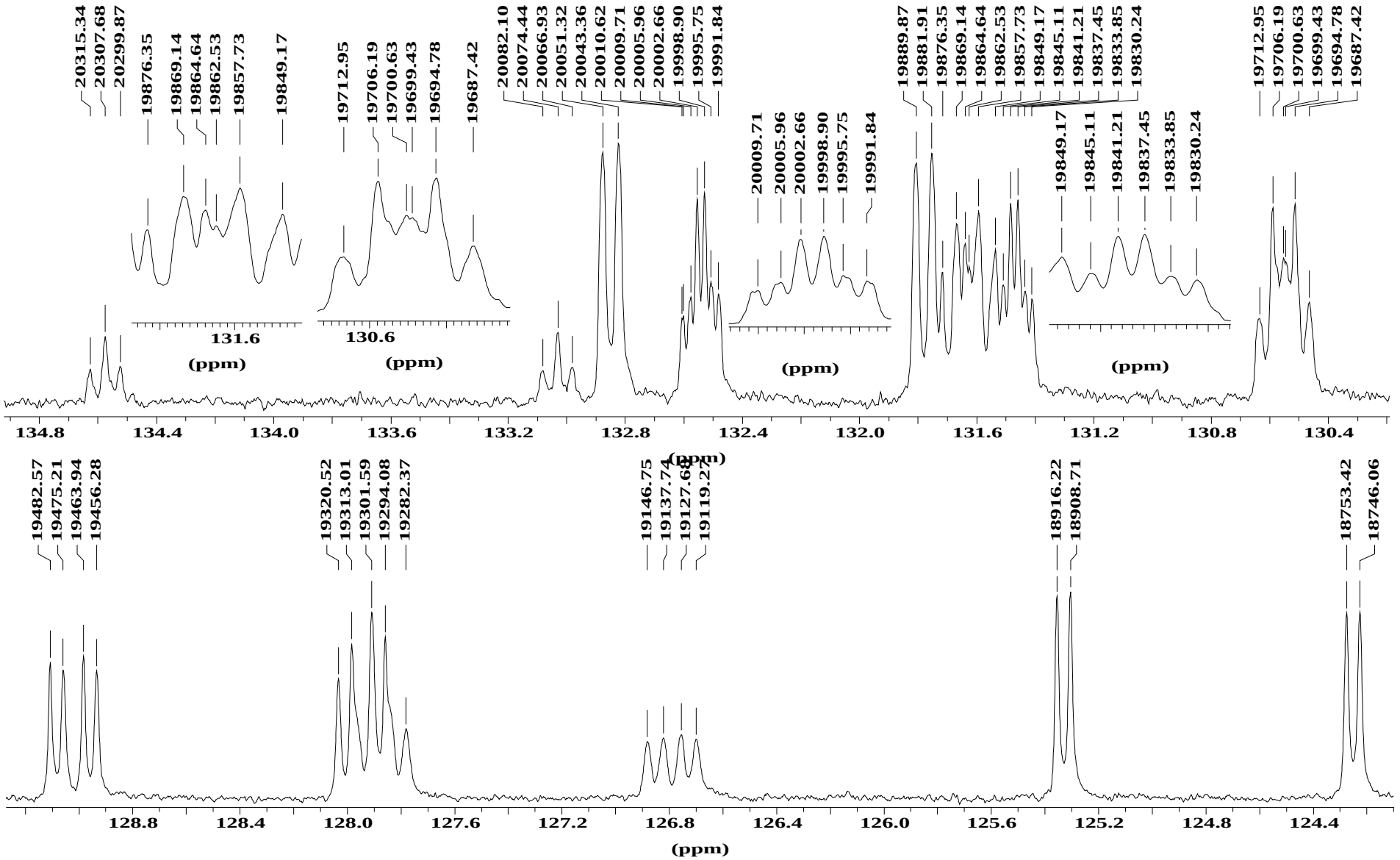

Fig. 4. Fragments of ^{13}C NMR spectra of compound **5** (150.9 MHz, $CDCl_3$).

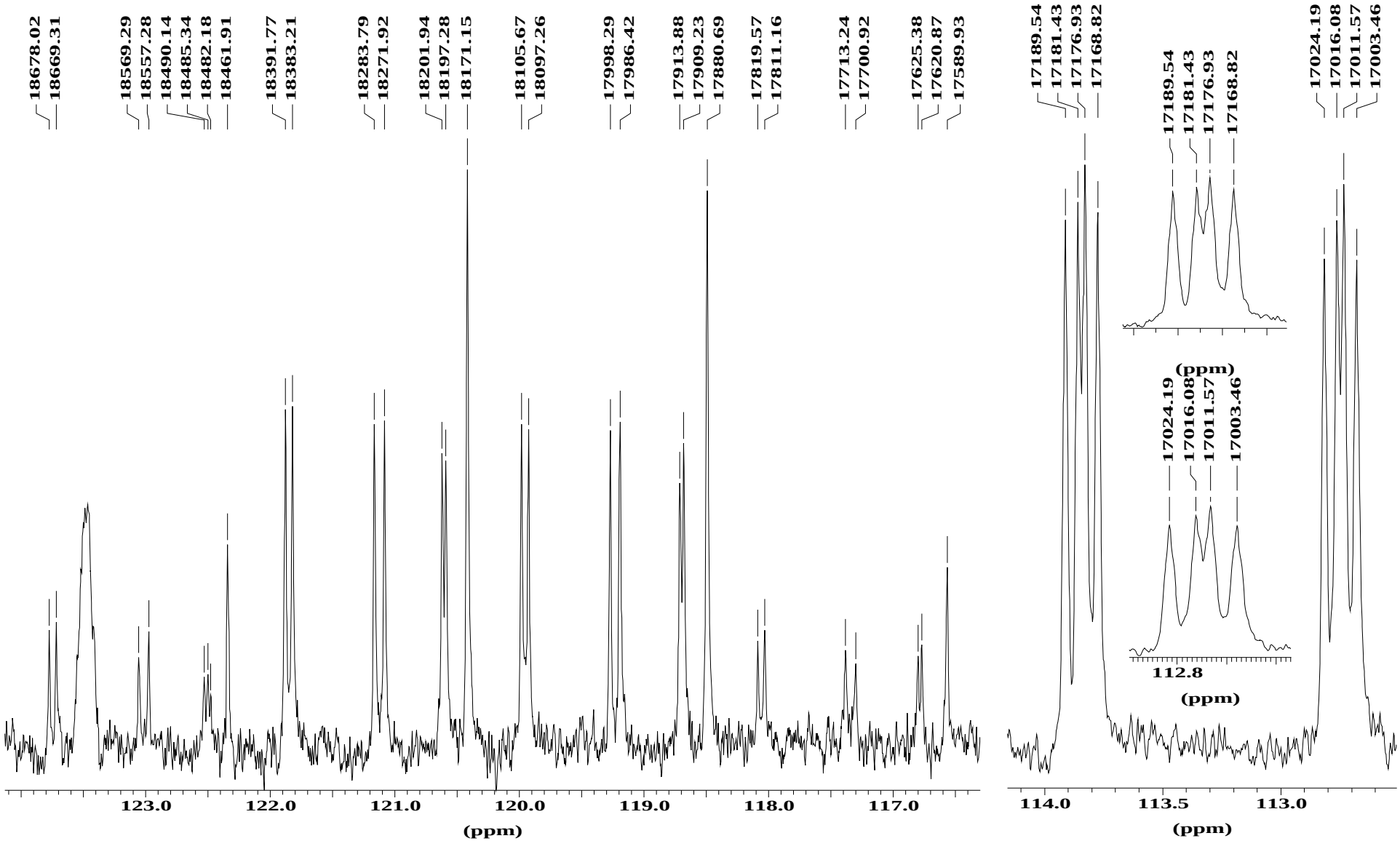

Fig. 5. Fragments of ^{13}C NMR spectra of compound **5** (150.9 MHz, $CDCl_3$).

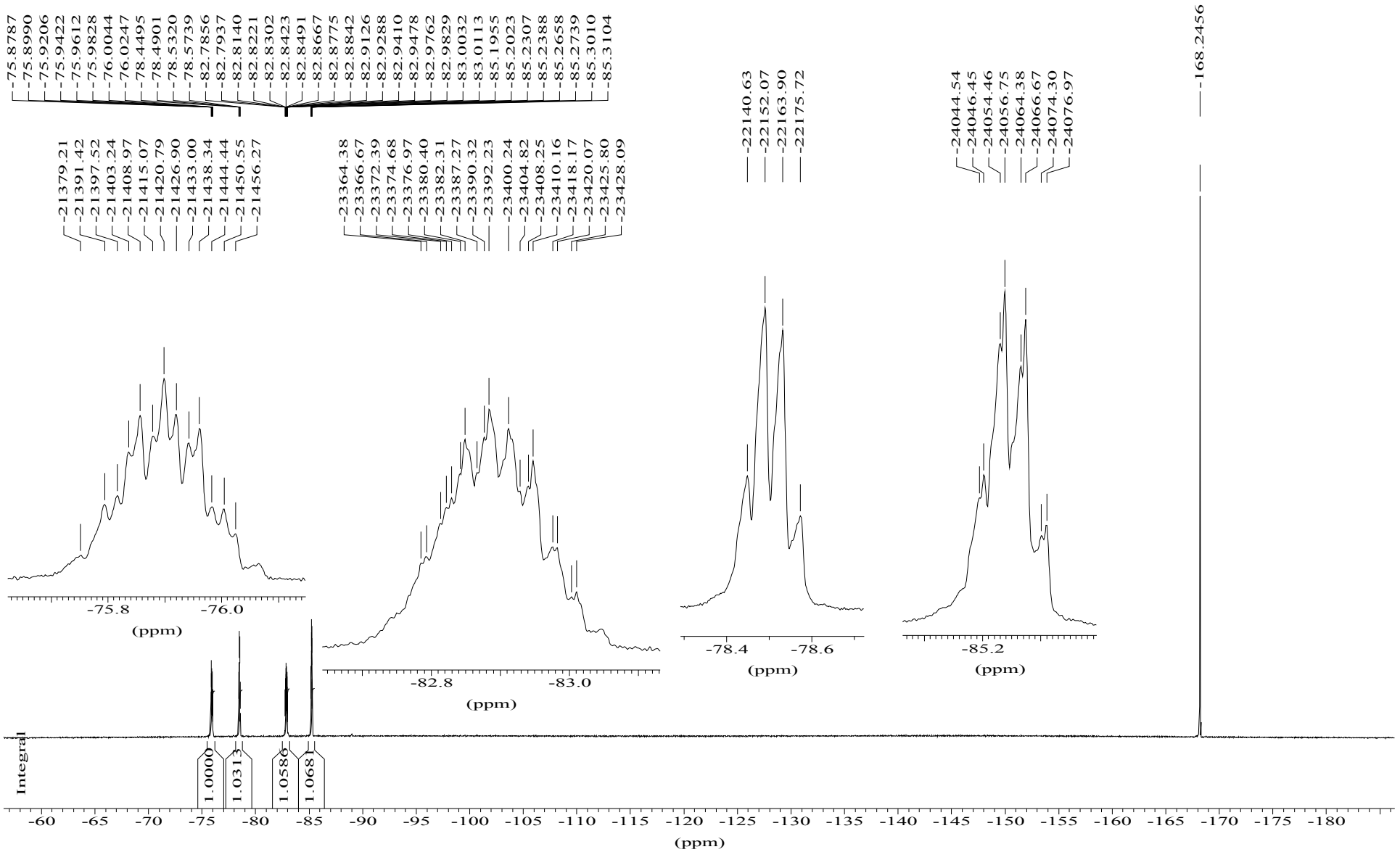

Fig. 6. ^{19}F NMR spectrum of compound **5** (282.64MHz, $CDCl_3$).

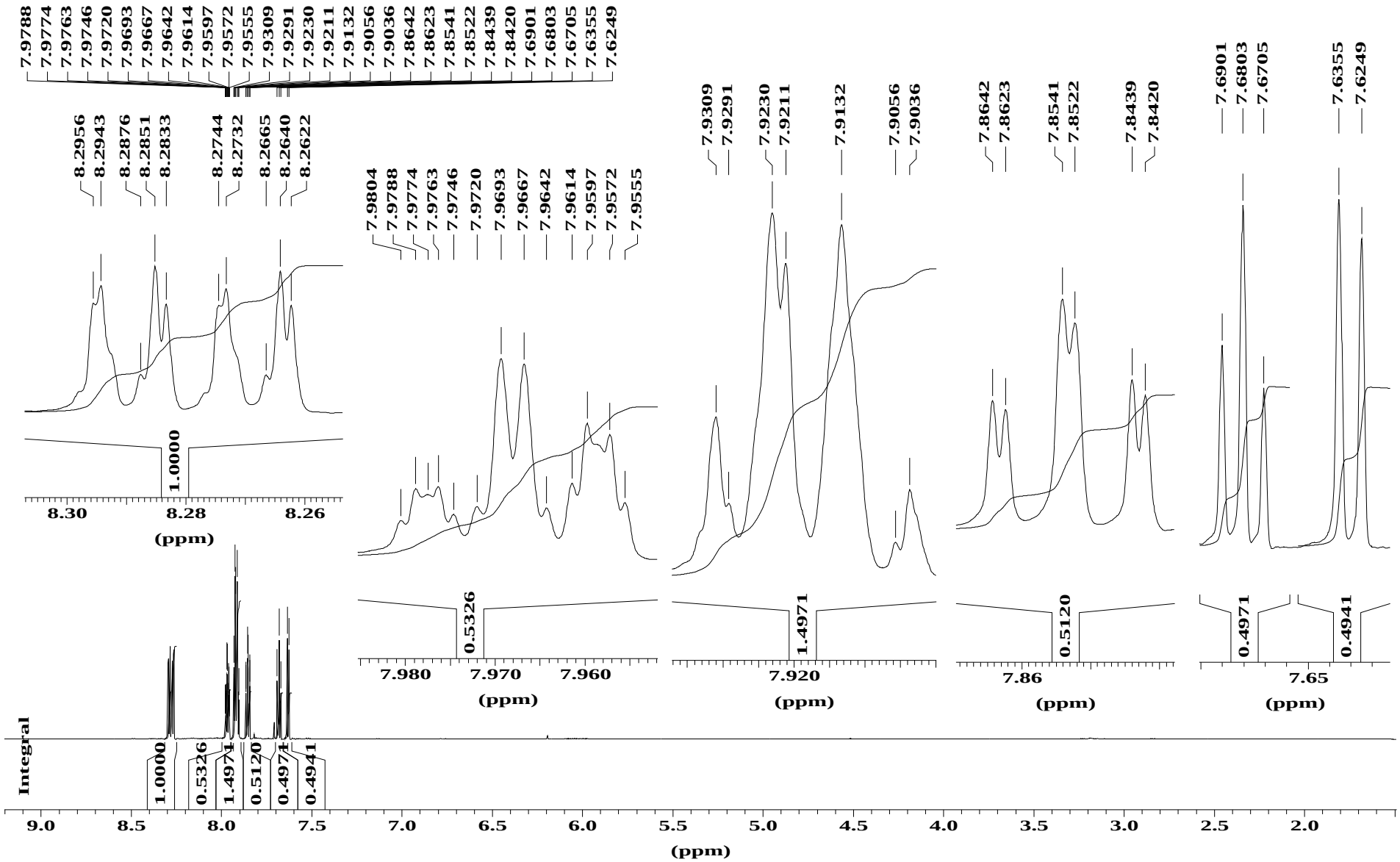

Fig. 7. ^{1}H NMR spectrum of compound **5** (600 MHz, $CDCl_3$).

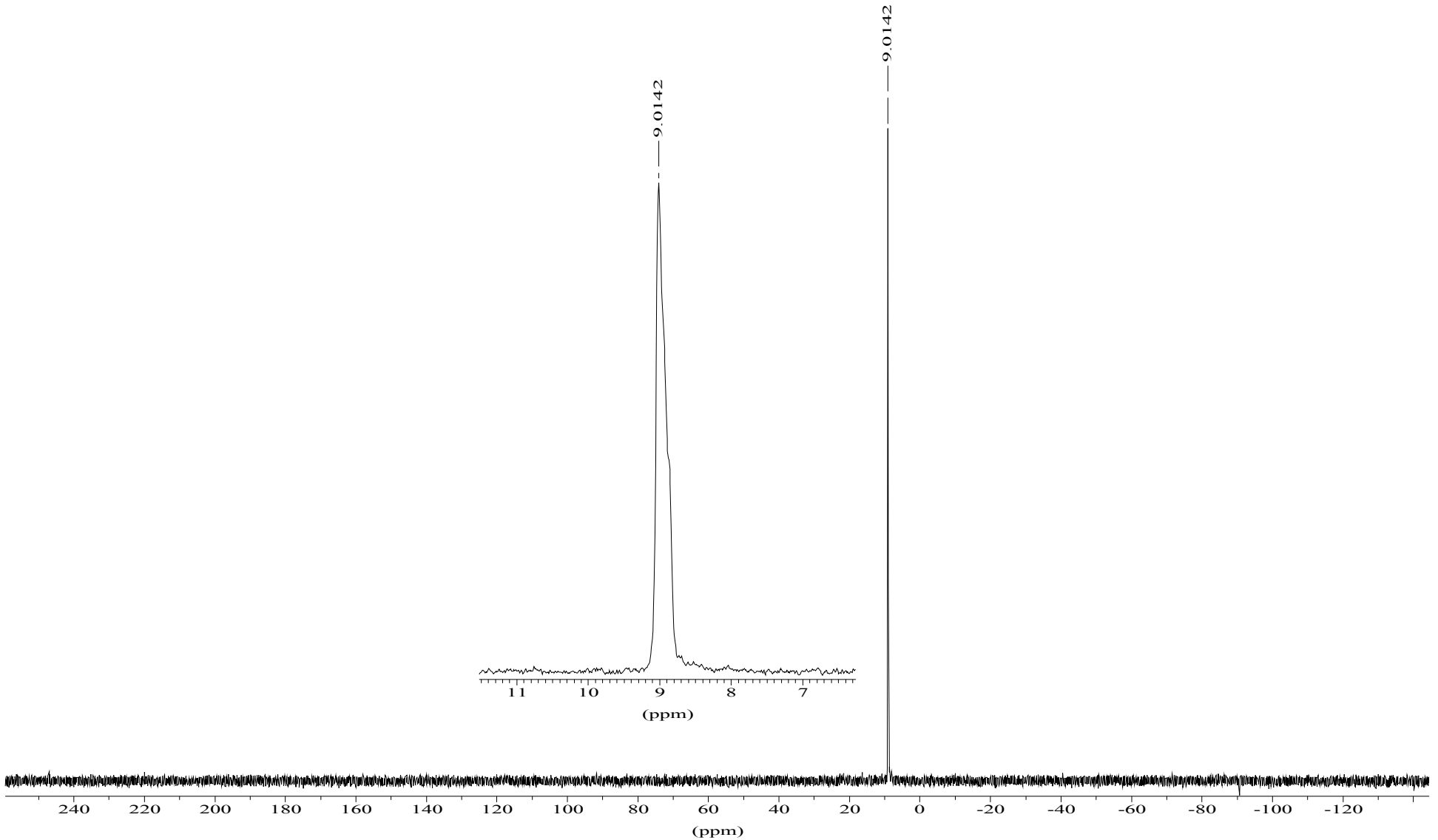

Fig. 8. ^{31}P-{^{1}H} NMR spectrum of compound **5** (242.8 MHz, $CDCl_3$).

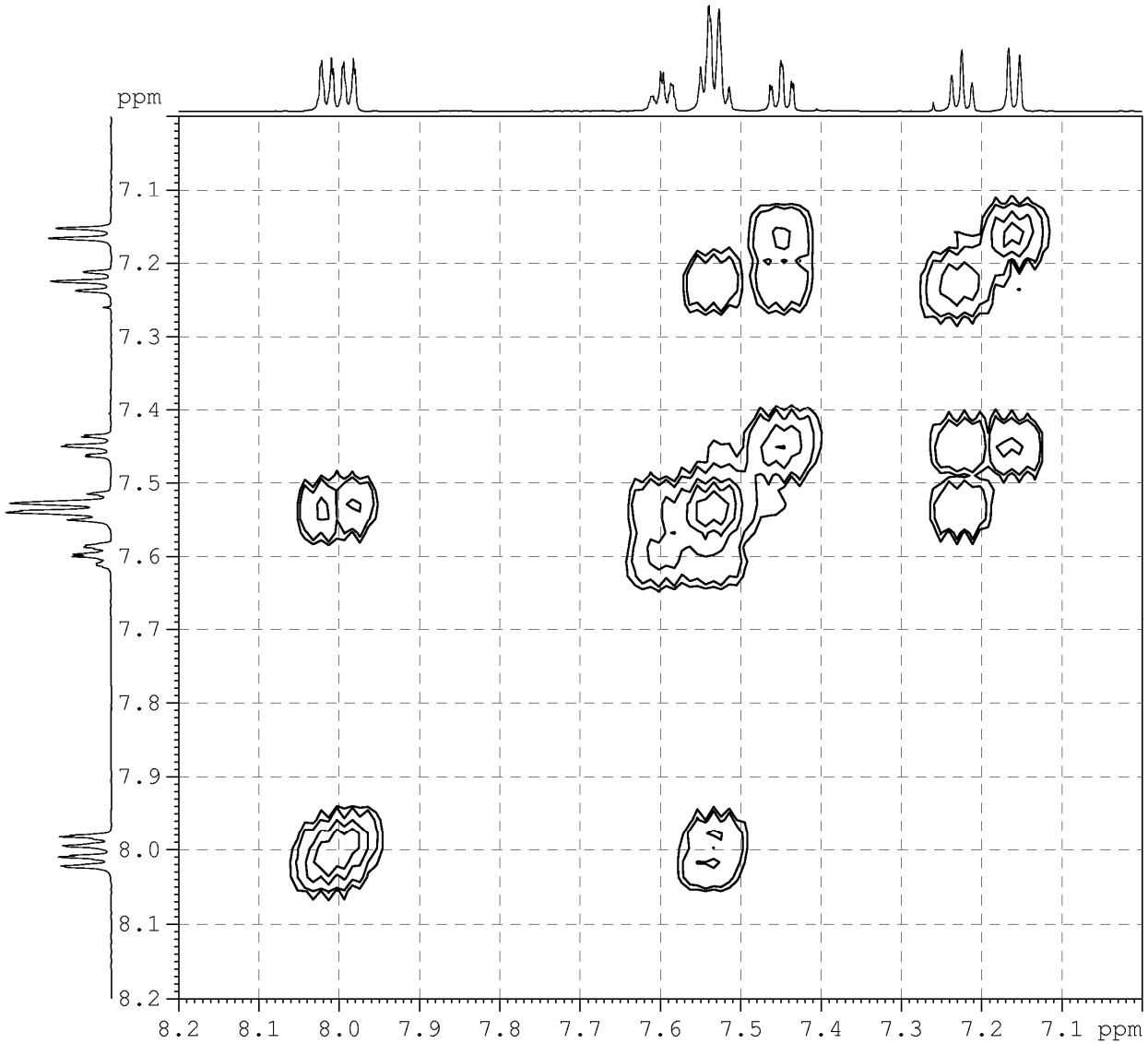

Fig. 9. ^{1}H-^{1}H COSY spectrum of compound **5** (600.000 MHz in ^{1}H, 150.864 MHz in ^{13}C, T = 303°K, $CDCl_3$).

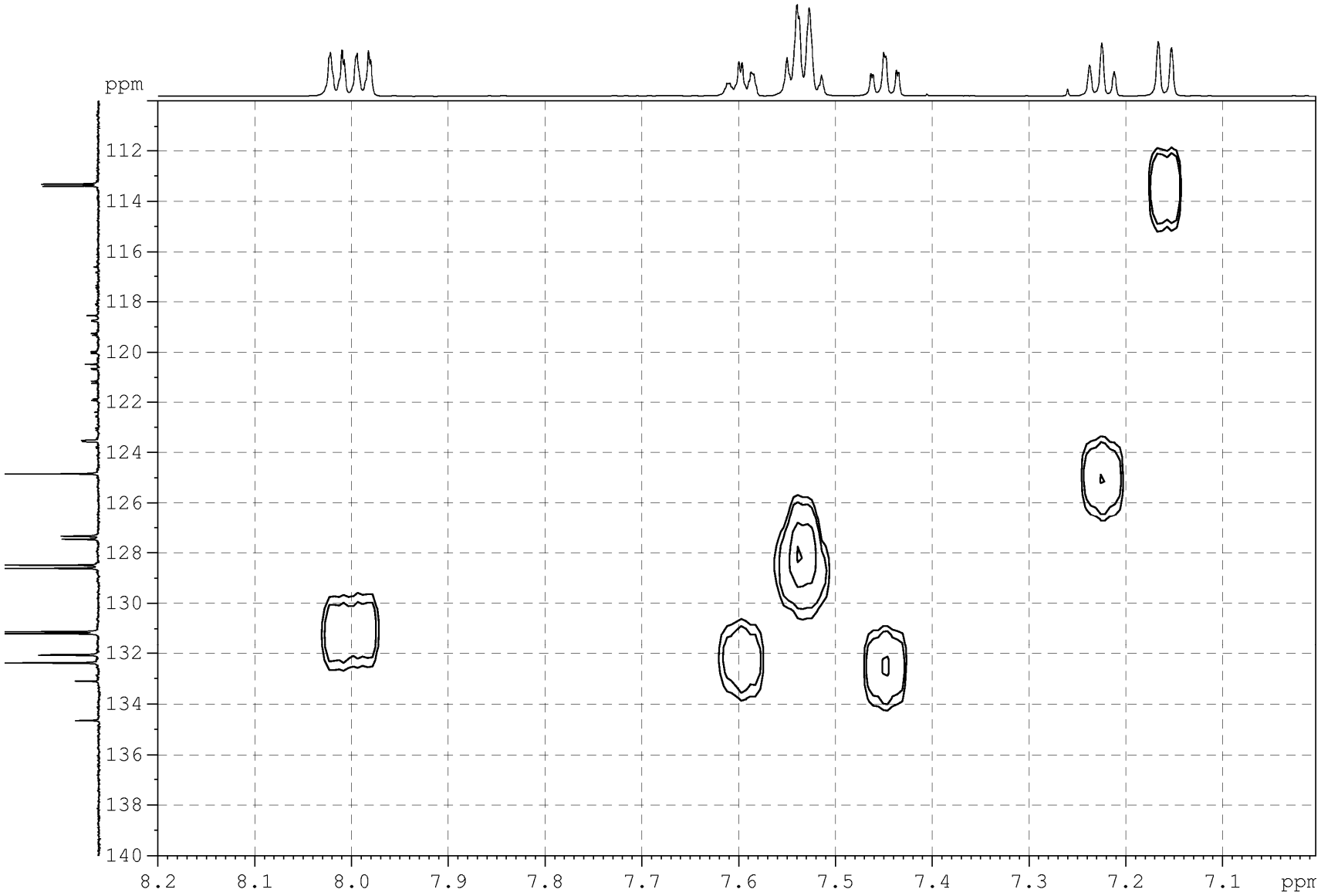

Fig. 10. ^{1}H-^{13}C HSQC spectrum of compound **5** (600.000 MHz in ^{1}H, 150.864 MHz in ^{13}C, T = 303°K, $CDCl_3$).

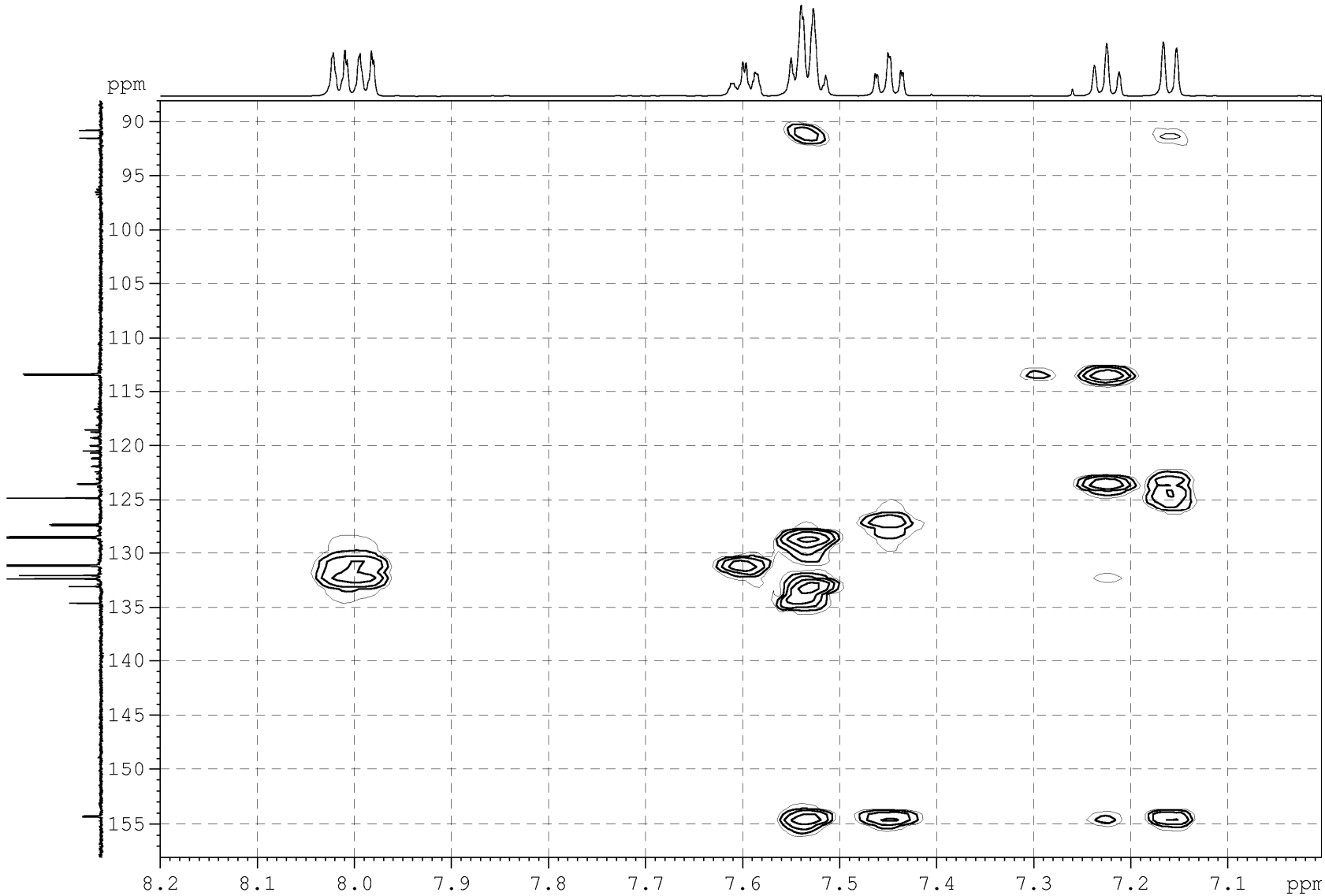

Fig. 11. ^{1}H-^{13}C HMBC spectrum of compound **5** (600.000 MHz in ^{1}H, 150.864 MHz in ^{13}C, T = 303°K, $CDCl_3$).

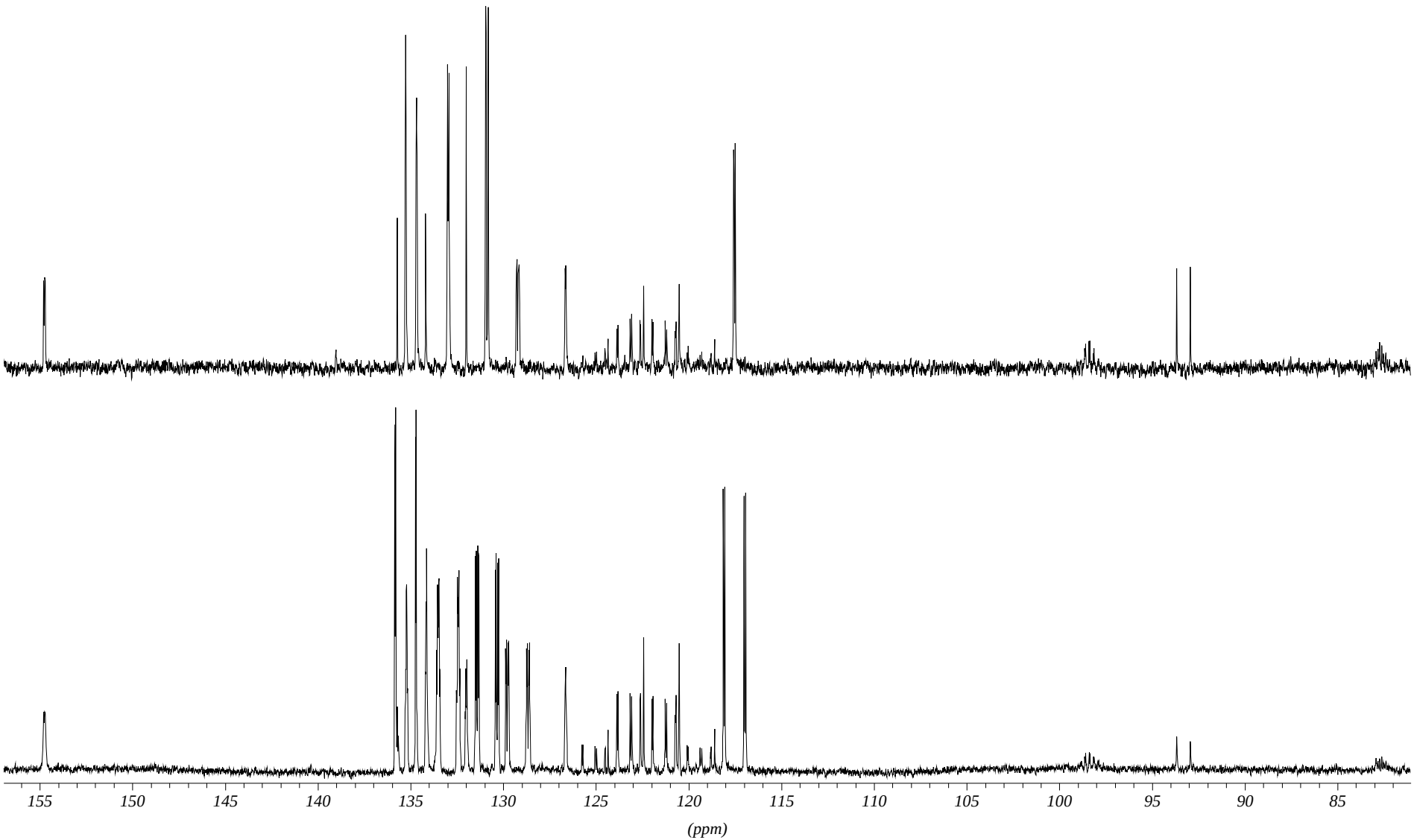

Fig. 12. ^{13}C-{^{1}H} and ^{13}C NMR spectra of compound **6** (150.9 MHz, acetone-D_6).

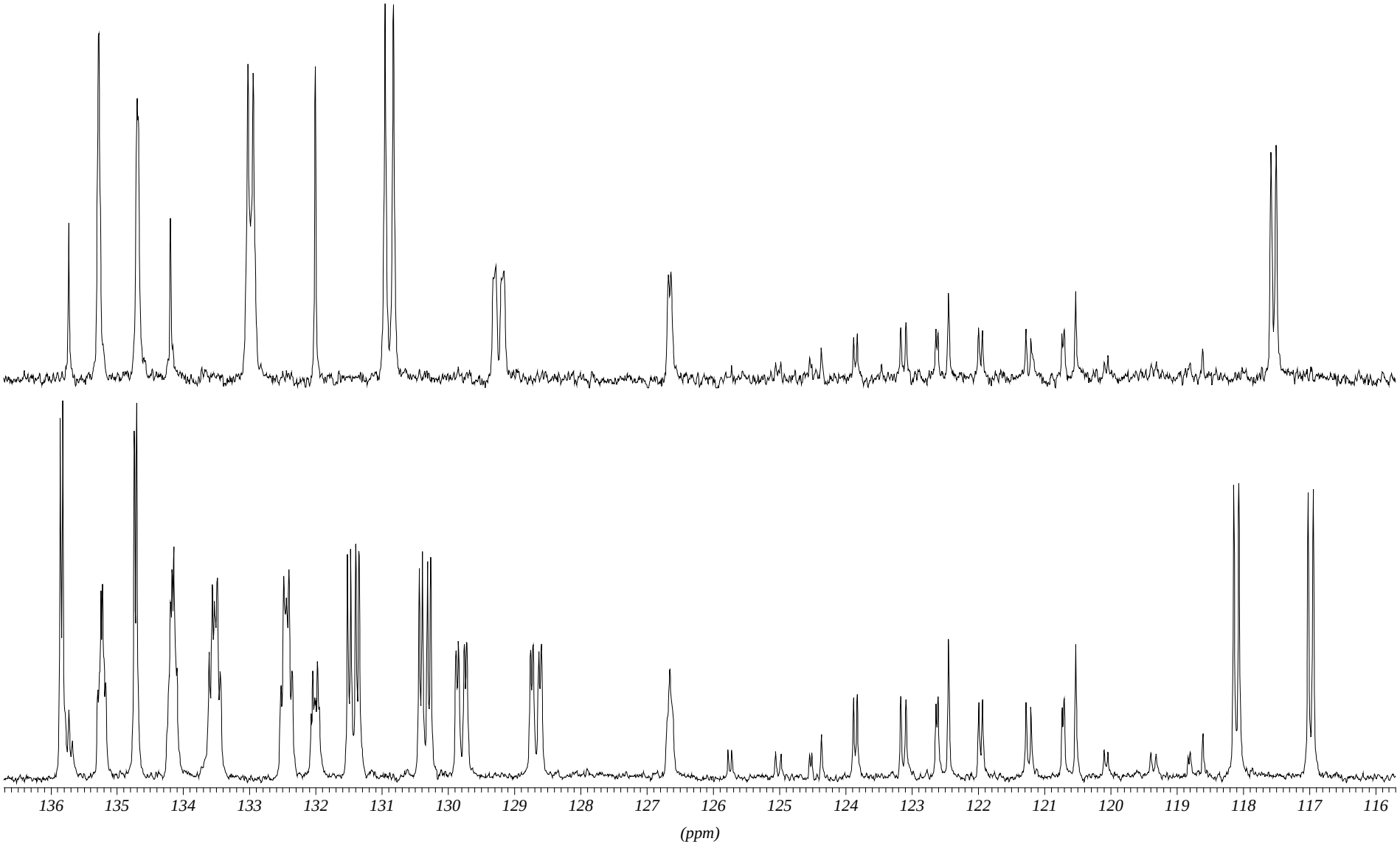

Fig. 13. Fragments of ^{13}C-{^{1}H} and ^{13}C NMR spectra of compound **6** (150.9 MHz, acetone-D_6).

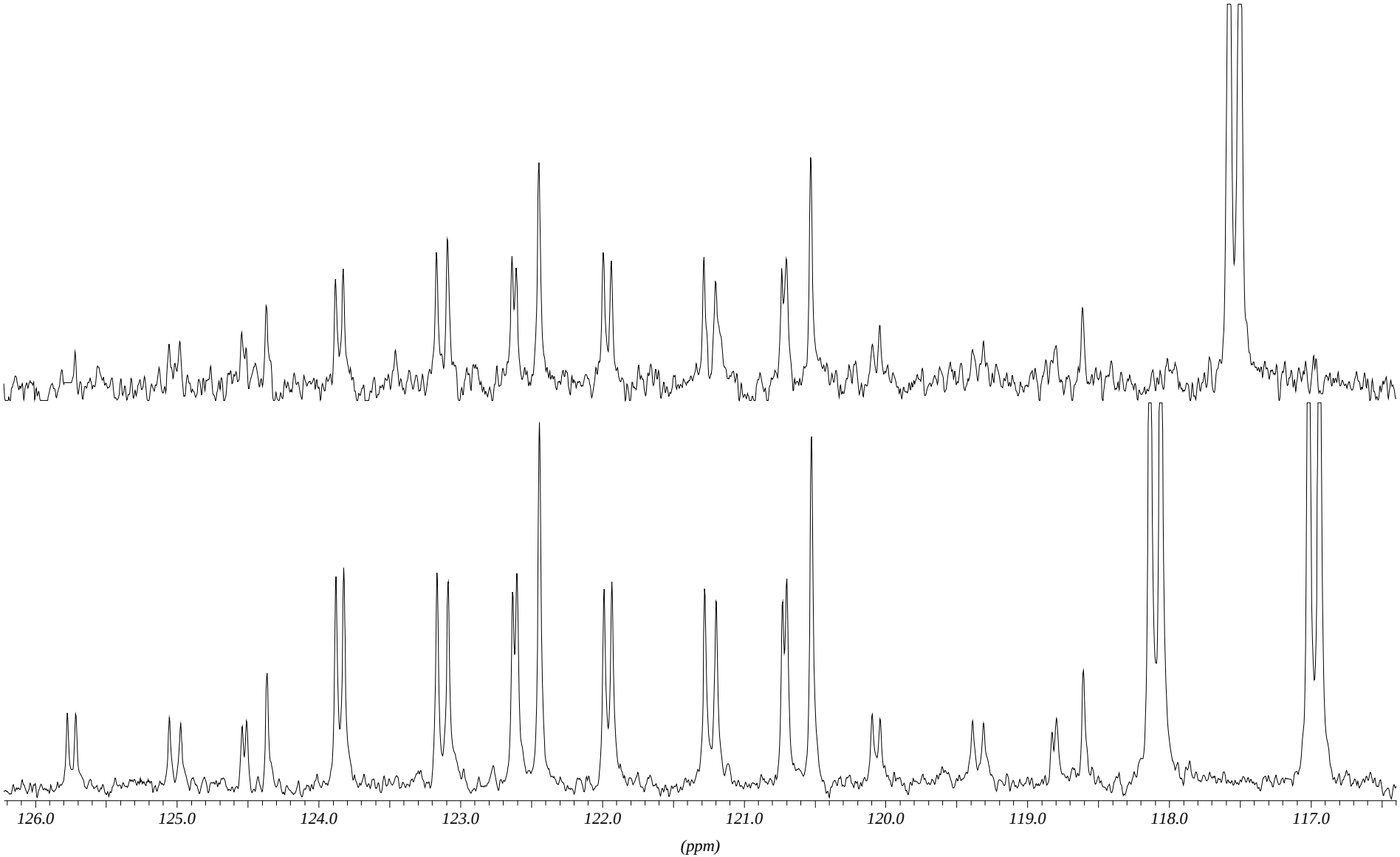

Fig. 14. Fragments of ^{13}C-{^{1}H} and ^{13}C NMR spectra of compound **6** (150.9 MHz, acetone-D_6).

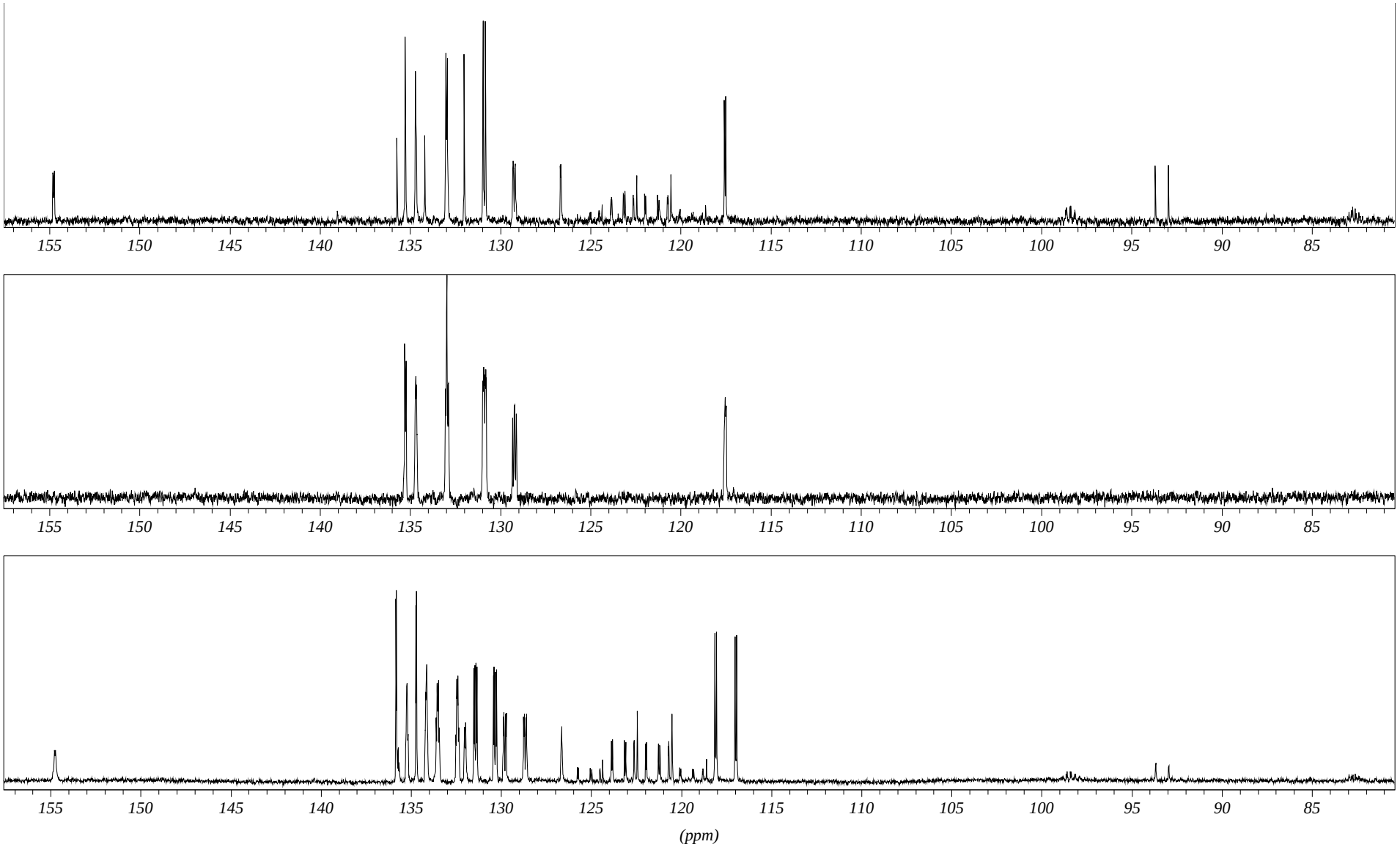

Fig. 15. ^{13}C-{^{1}H}, DEPT, ^{13}C and NMR spectra of compound **6** (150.9 MHz, acetone-D_6).

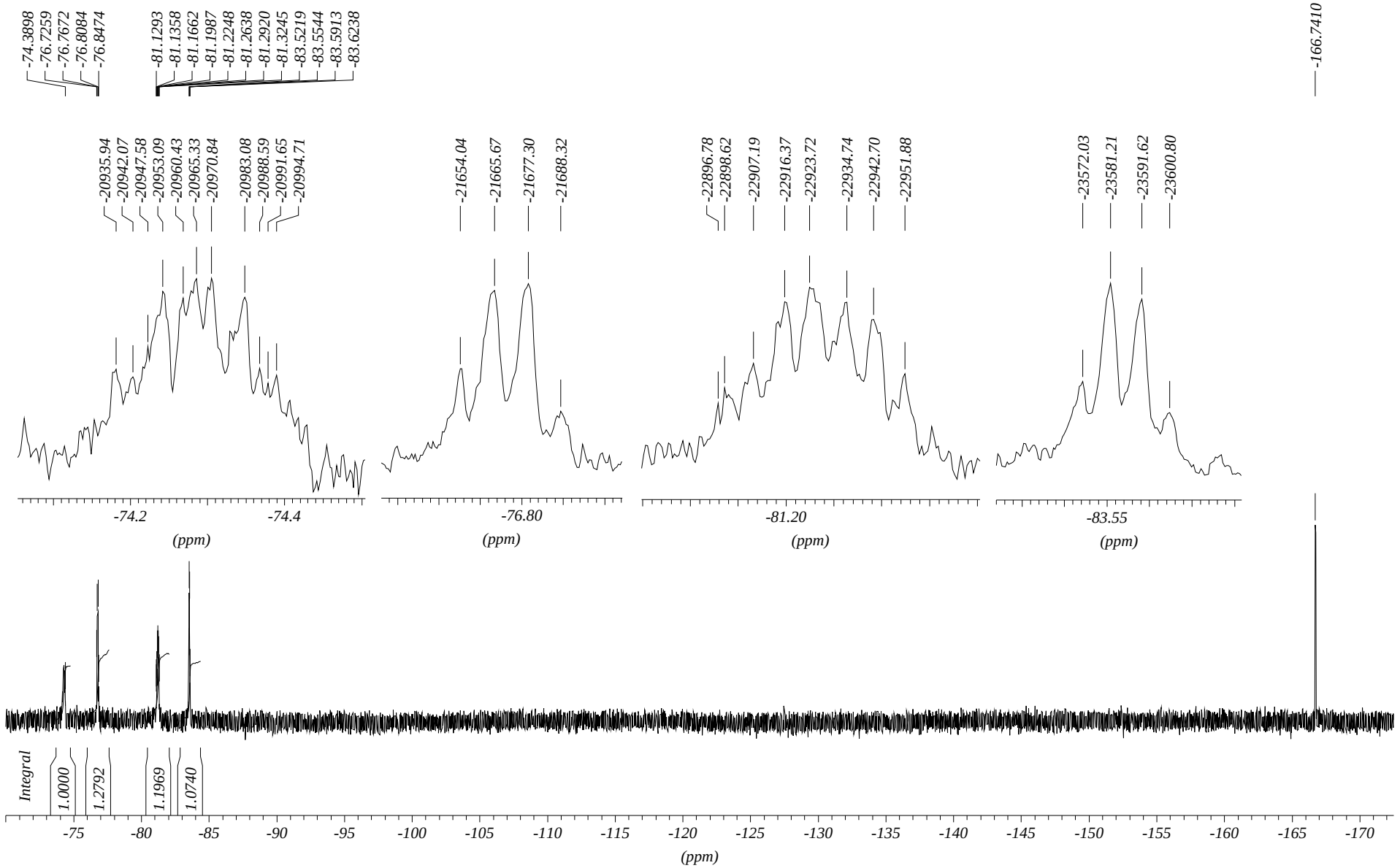

Fig. 16. ^{19}F NMR spectrum of compound **6** (282.64MHz, acetone-D_6).

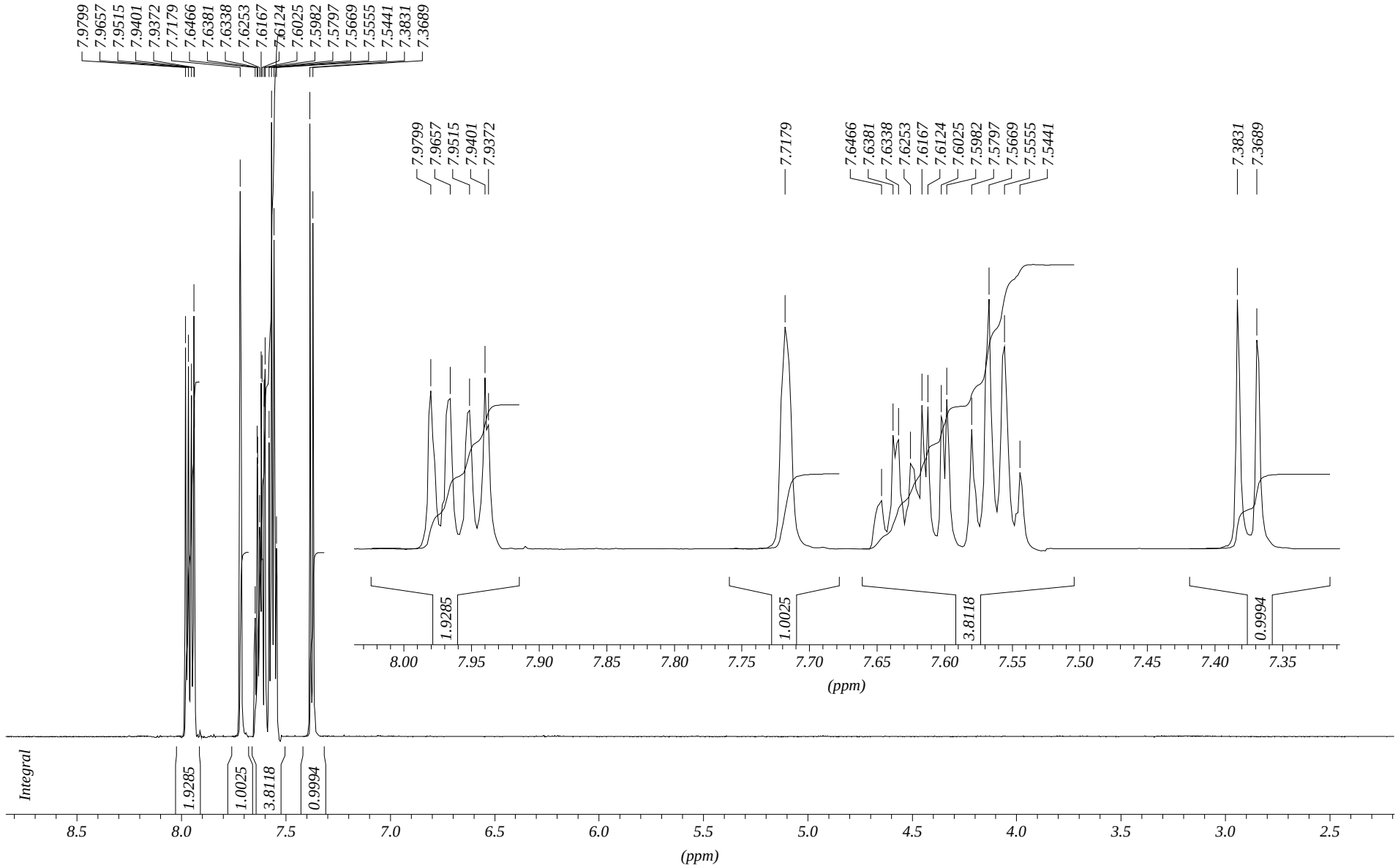

Fig. 17. ^{1}H NMR spectrum of compound **6** (600 MHz, $CDCl_3$).

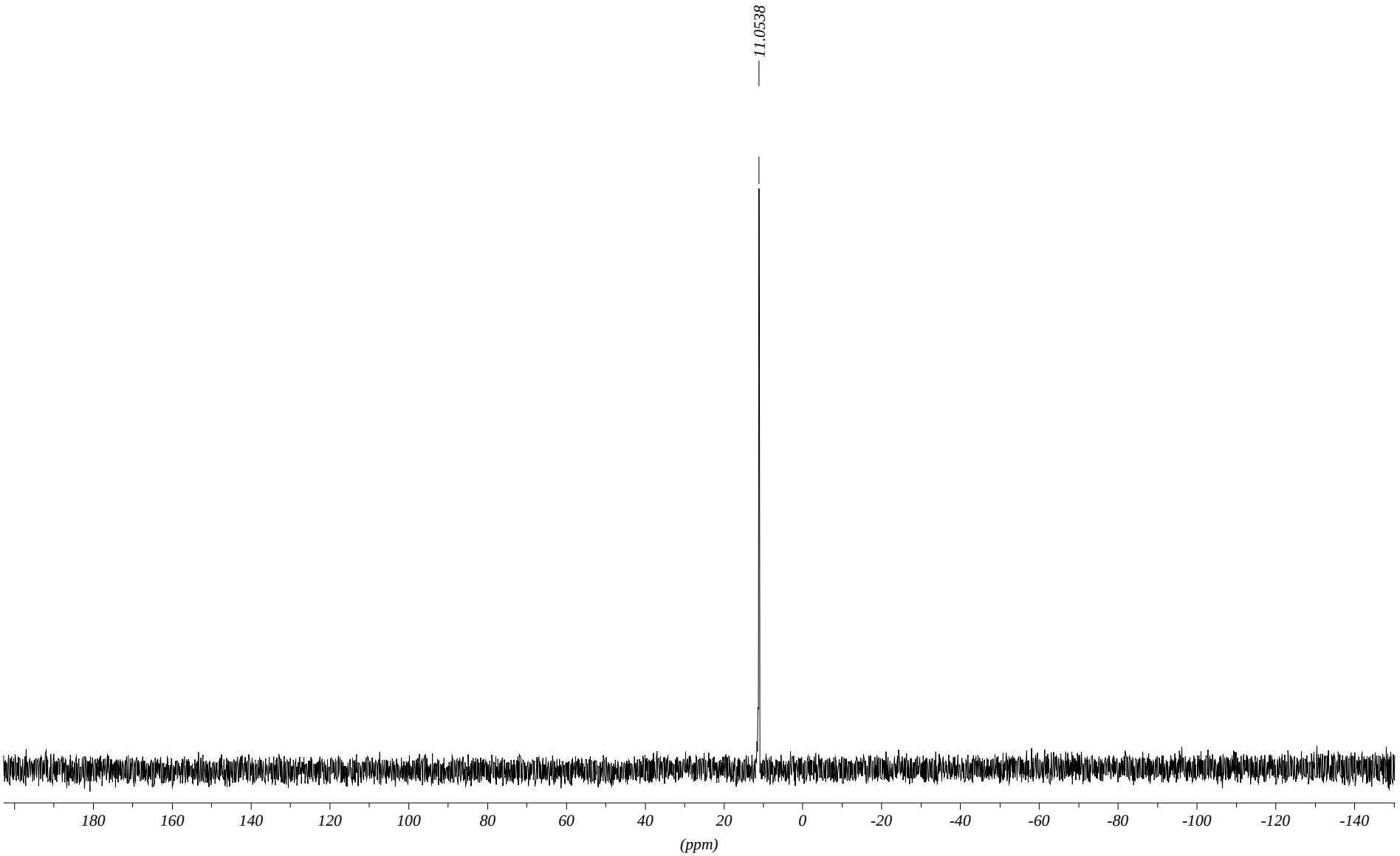

Fig. 18. ^{31}P-{^{1}H} NMR spectrum of compound **6** (242.8 MHz, acetone-D_6).